SYNTHESIS AND ACID-BASE TRANSFORMATIONS OF 8-SUBSTITUTED 10-PHENYL-10-HYDROXY-10H-PYRIDO[2,3-b]CHROMENES

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The corresponding 2-(p-substituted phenoxy)-3-aroylpyridines were obtained by the reaction of 2-(p-substituted phenoxy)nicotinonitriles with phenylmagnesium bromide. It is shown that they are readily cyclized to 8-substituted 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes by the action of concentrated sulfuric acid in glacial acetic acid. The pK_R + values of the cyclization products, which range from -7.70 to -10.83 and correlate with the σ_p° substituent constants, were determined by spectrophotometry.

In developing our earlier research [1] we have accomplished the synthesis of 8-substituted 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes in order to study the acid-base transformations and the possibilities of synthesis on the basis of 2-aryloxy-3-benzoylpyridines.



2-Aryloxy-3-benzoylpyridines (IIa-e, Table 1) are formed in the reaction of 2-aryloxynicotinonitriles (Ia-d, Table 1) with phenylmagnesium bromide. The IR spectra of IIa-e contain a band of stretching vibrations of a carbonyl group at 1690 cm⁻¹ but, in contrast to the spectra of starting Ia-d, do not contain a band of a CN group.

The cyclization of ketones IIa-e proceeds smoothly when acetic acid solutions of them are treated with excess concentrated sulfuric acid at room temperature or upon heating to 100°C. The reaction is completed more rapidly when electron-donor substituents are present in the phenoxy group and more slowly when electron-acceptor substituents are present. The fact of the cyclization of ketones IIa-e to pyrido[2,3-b]chromene derivatives is confirmed by data from the IR spectra (stretching vibrations of a hydroxy group at 3590 cm⁻¹) and also by a comparison of samples of IIIa obtained by this method and previously described methods [1].

Pyrido[2,3-b]chromenes IIIa-e (Table 1) are colorless crystalline substances, and bands with maxima at 270 and 285 nm and bands at 220 nm are observed in their UV spectra in ethanol. A bathochromic shift of the bands occurs in the spectra of these compounds in sulfuric acid solutions at low concentrations, while maxima appear at 367 and 490 nm in concentrated acid. On the basis of these changes in analogy with [1] one should acknowledge that IIIa-e in sulfuric acid undergo stepwise ionization to give successively ions A and B.

A linear relationship between the logarithms of the indicator ratios (log Q) and the H_R values [2], which characterize the acidities of the media, is observed. The slopes of this relationship range from 0.53 to 0.63, i.e., the A \Rightarrow B equilibrium is complicated by an additional (probably solvation) effect.

The constants of the A \rightleftharpoons B equilibrium in sulfuric acid-water were determined by spectrophotometry. The pK_R+ values that characterize this equilibrium range from -7.70 to -10.83

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Com- pound	R	mp, °C	Found C H	, % Hal	N	Empirical formula	Ca] c	cula н	ated, Hal	<i>¶</i> N	Yield, %
la Ib Ic Id Ila Ilc I d Ile Illa Illa Illo Illa Illo Illa Illo Illo	CH ₃ Br Cl F H CH ₃ Br Cl F H CH ₃ Br Cl F	$\begin{array}{c} 106-107\\ 112-113\\ 105-106\\ 95-96\\ 80-82\\ 90-91\\ 92-93\\ 86-87\\ 86-87\\ 228-229*\\ 233-234\\ 247-248\\ 236-237\\ 219-220\\ \end{array}$	74,1 4,7 	29,2 15,4 22,7 11,3 22,9 11,6 	$\begin{array}{c} 13,5\\10,2\\12,2\\5,0\\3,9\\4,5\\4,8\\5,1\\4,7\\4,0\\4,7\\4,9\end{array}$	$\begin{array}{c} C_{13}H_{10}N_2O\\ C_{12}H_7BrN_2O\\ C_{12}H_7CIN_2O\\ C_{12}H_7FN_2O\\ C_{18}H_{13}NO_2\\ C_{19}H_{15}NO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}FNO_2\\ C_{18}H_{12}FNO_2\\ C_{18}H_{13}NO_2\\ C_{19}H_{15}NO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}BrNO_2\\ C_{18}H_{12}FNO_2\\ C_{18}H_{18}H_{18}FNO_2\\ C_{1$	74,3 — 78,5 78,9 — 78,5 78,9 — 78,5 78,9 — —	4,8 	 29,0 15,4 22,6 11,4 22,6 11,4 22,6 11,4 	$13,3 \\ 10,2 \\ 12,1 \\ 13,1 \\ 5,1 \\ 4,8 \\ 3,9 \\ 4,5 \\ 4,8 \\ 5,1 \\ 4,8 \\ 5,1 \\ 4,8 \\ 5,4 \\ 4,8 \\ $	77 80 74 55 43 42 52 53 54 72 73 72 88 75

TABLE 1. Characteristics of the Synthesized Compounds

*A melting point of 215-216°C was erroneously presented in [1].

TABLE 2. Parameters of Correlation of the Logarithms of the Indicator Ratios with H_R and pK_R + of 8-Substituted 10-Phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes

Com - pound	R	λ _{max} ,* nm	lg e	H _R interval	-pK _R +	r	s
IIIa LIIb IIIc IIId IIIe	H CH₃ Br Cl F	367 380 381 381 372	4,53 4,51 4,54 4,54 4,51	8,09-9,47 7,06-8,64 10,02-11,40 10,02-11,40 10,00-10,90	$8,87 \pm 0,27$ 7,70 $\pm 0,20$ 10,83 $\pm 0,27$ 10,83 $\pm 0,27$ 10,58 $\pm 0,15$	0,997 0,999 0,998 0,998 0,998 0,998	0,033 0,013 0,018 0,015 0,012

*Data for solutions of pyridinium-benzopyrylium salts of the B type in 96% sulfuric acid are presented.

(Table 2) and correlate with the σ_p° substituent constants ($\rho = -7.71$, $pK_{Rcalc} \circ = -8.91$, r = 0.990, s = 0.17). This correlation constitutes evidence that the effect of substituents on the reaction center is realized primarily via an inductive mechanism. The reaction constant exceeds the ρ value of series of similar compounds with substituents in the phenyl ring (see [1]) by a factor greater than two. This should be explained by the fact that the substituent in IIIa-e is located directly in the benzopyrylium ring, in which the positive charge is concentrated, and readily transmits electronic effects to it.

EXPERIMENTAL

The IR spectra of solutions of IIa-e in CCl₄ and of IIIa-e in CHCl₃ were recorded with a UR-20 spectrometer. The UV spectra were determined with a Spectromom-202 spectrophotometer. The ionization constants were determined by a spectrophotometric method with the same spectrophotometer using $2 \cdot 10^{-5}$ M solutions at 20 ± 1°C. The analytical line corresponded to the maximum at 367-381 nm. The equation pK_R = H_R + log [B]/[A] was used to find the pK values.

2-(p-Substituted phenoxy)nicotinonitriles (Ia-d). A mixture of 0.06 mole of 2-chloronicotinonitrile [3] and 0.1 mole of the corresponding p-substituted sodium phenoxide in 10 g of the corresponding phenol was heated at 140°C for 30 min, after which it was poured into water, and the resulting precipitate was triturated with 10% NaOH, removed by filtration, and crystallized from ethanol to give Ia-d.

2-(p-Substituted phenoxy)-3-benzoylpyridines (IIa-d). An ether solution of 0.02 mole of 2-phenoxynicotinonitrile [4] or 2-(p-substituted phenoxy)-nicotinonitriles Ia-d was added to 0.04 mole of phenylmagnesium bromide in 30 ml of ether, and the mixture was heated for 6 h. It was then decomposed with a saturated solution of NH₄Cl, and the ether layer was separated and treated with steam. The residue was crystallized from methanol to give IIa-e.

<u>8-Substituted 10-Pheny1-10-hydroxy-10H-pyrido[2,3-b]chromenes (IIIa-e)</u>. A 20-ml sample of concentrated H_2SO_4 was added to a solution of 3.5 mmole of IIa-e in 10 ml of acetic acid, and the mixture was heated on a water bath for 6 h. It was then poured into water, and the

aqueous mixture was neutralized with Na_2CO_3 . The precipitate was removed by filtration and crystallized from ethanol to give IIIa-e.

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF

HETARYLETHYLENE DERIVATIVES OF 2,5-DIPHENYLOXAZOLE

AND 2,5-DIPHENYL-1,3,4-OXADIAZOLE

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A number of new organic luminophores was synthesized by PO olefination from 2-(4'-bromomethylphenyl)-5-phenyloxazole and -1,3,4-oxadiazole and various heterocyclic aldehydes that contain a furan ring. The absorption and fluorescence spectra of the products in toluene, as well as their scintillation characteristics, were measured. The effect of the electronic nature of the substituents on the spectral-luminescence properties of the luminophores is discussed.

The synthesis of organic luminophores with various structures among arylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole (I) has demonstrated the possibility of the preparation of intensely luminescing substances that have found the most diverse application [1-5].



The present communication is devoted to the synthesis and investigation of the fluorescence and scintillation properties of hetarylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyloxadiazole (II, III) that have more complex structures and contain a furan ring.



The synthesis of II and III was accomplished by PO olefination, which usually leads to the trans isomers [6]. The starting compounds were 2-(4'-bromomethylphenyl)-5-phenyloxazole or -1,3,4-oxadiazole and the corresponding substituted 5-arylfurfural.

The structures of the compounds obtained were confirmed by data from the IR spectra, in which out-of-plane deformation vibrations of the hydrogen atoms of the trans-vinylene group at $955-970 \text{ cm}^{-1}$ and the characteristic frequencies of the furan ring appear.

The results of an investigation of the spectral-luminescence properties of the products in toluene are presented in Tables 1 and 2.

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